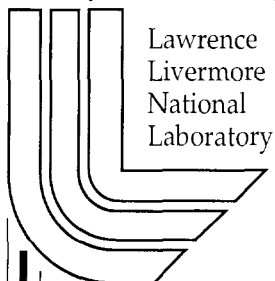


Preparation of NIF Scale Poly(α -Methylstyrene) Mandrels

*M. Takagi, R. Cook, B. McQuillan, F. Elsner, R. Stephens,
A. Nikroo, J. Gibson, S. Paguio*

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PREPARATION OF NIF SCALE POLY(α -METHYLSTYRENE) MANDRELS

Masaru Takagi, Robert Cook
Lawrence Livermore National Laboratory
Livermore, CA 94550

Barry McQuillan, Fred Elsner, Richard Stephens,
Abbas Nikroo, Jane Gibson and Sally Paguio
Fusion Group, General Atomics
San Diego, CA 92121

I. INTRODUCTION

All planned National Ignition Facility¹ (NIF) capsule targets except machined beryllium² require a plastic mandrel upon which the ablator³ is applied. This mandrel must at least meet if not exceed the symmetry and surface finish requirements⁴ of the final capsule. The mandrels are produced by a two-step process.⁵ In the first step a thin-walled poly(α -methylstyrene)(P α MS) shell is produced using microencapsulation techniques.⁶ This shell is overcoated with 10 to 15 μ m of glow discharge polymer⁷ (GDP) and then pyrolyzed at 300 °C. This pyrolysis causes the P α MS to depolymerize to gas phase monomer that diffuses away through the more thermally stable plasma polymer shell, which retains all the symmetry of the original P α MS shell. Thus our challenge has been to produce 2-mm-diameter P α MS shells to serve as these initial “decomposable” mandrels that meet or exceed the current NIF design specifications.

The basic microencapsulation process used in producing P α MS mandrels involves using a droplet generator to produce a water droplet (W1) encapsulated by a fluorobenzene solution of P α MS (O), this compound droplet being suspended in a stirred aqueous bath (W2). Historically this bath has contained poly(vinyl alcohol) (PVA, 88% hydrolyzed, mol. wt. ~25,000 g/mol) to prevent agglomeration of the initially fluid compound droplets. As the compound droplets are stirred in the bath, the fluorobenzene solvent slowly dissipates leaving a solid P α MS shell. The internal water is subsequently removed by low temperature drying. We found using these techniques that 2-mm shells could easily be produced, however their low mode sphericity did not meet design specifications. In our last published report⁸ we detailed how replacement of the PVA with poly(acrylic acid) (PAA) resulted in a major improvement in sphericity due to a greatly increased interfacial tension between the bath and the compound droplet, relative to the use of PVA as the bath additive. P α MS mandrels produced using PAA in the bath along with slow curing to suppress Marangoni convection that was perturbing the mode 10 to 20 symmetry⁹ resulted in 2-mm-diameter P α MS shells with mode 2 out-of-round¹⁰ (OOR) of ~0.5 μ m (as well as non-concentricity¹¹ (NC) < 1%) which meet the capsule design requirements. A representative set of equatorial traces produced by our AFM-based Spheremapper¹² along with the computed power spectrum is shown in Figure 1 for an average shell. Although the power spectrum is at or

below the design specification at nearly all modes one can see in the traces some degree of roughness which manifests itself at the very high modes in the power spectrum.

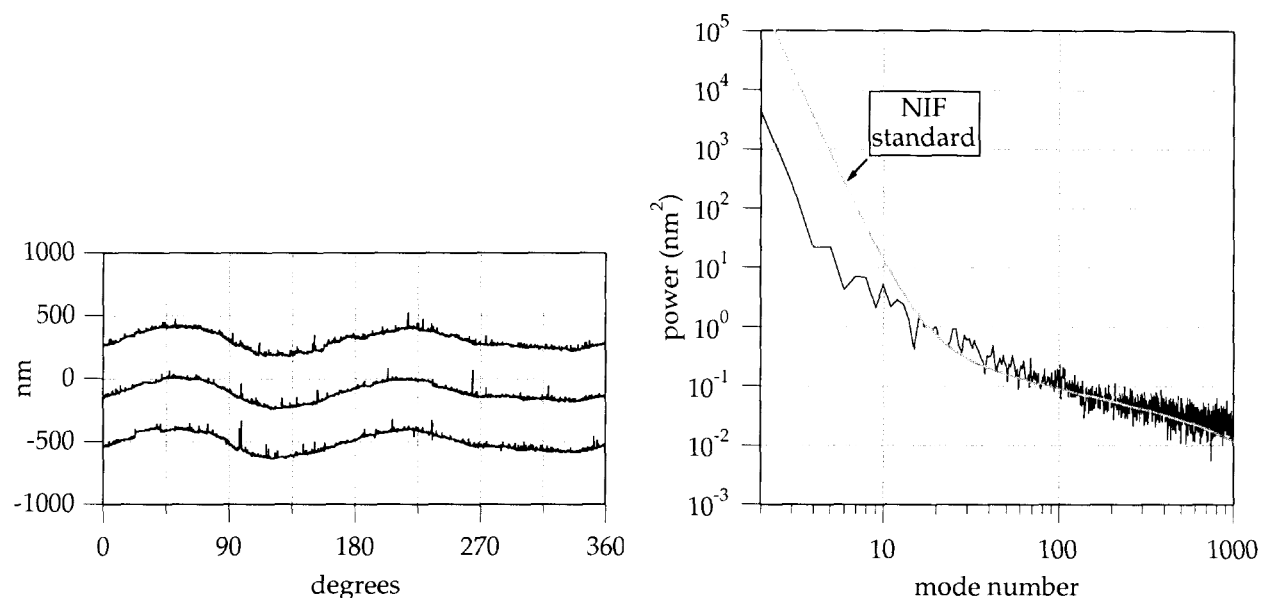


Figure 1. Shown are representative equatorial traces and the power spectrum from an average shell produced in PAA.

When these shells were overcoated with GDP prior to the pyrolysis step it was found that the resulting surface was covered with small domes. In Figure 2 we show a SEM image of a shell surface with a 55 μm GDP coating, and below it a set of representative equatorial traces and the resulting shell power spectrum. Clearly the high frequency roughness on the P α MS shell has seeded defect growth⁷ in the GDP layer, producing an unacceptable surface finish. This phenomenon does *not* occur when PVA is used in the bath, thus we concluded that the PAA was leaving a fine residue on the P α MS shell surface. Although the concentration of PAA used in the bath is very low (0.05 wt%) a combination of high molecular weight ($\sim 10^6$ g/mol) and strong intermolecular interactions result in facile gel formation,⁸ and in addition the material is very difficult to dissolve. We expect that the PAA aqueous bath solution may contain minute gel particles that are not captured by the 3 μm pore size filter used in preparing the solution. Attempts to use finer pore size filters were unsuccessful, resulting in vanishingly small filtration rates or simple clogging. Thus we believe that the residue on the P α MS shell surface was PAA which adsorbed onto, or became embedded in the surface during curing.

This report is an expansion of a paper that has been published in Fusion Technology.¹³ In what follows we will give a complete description of the microencapsulation methods used, along with process details that are not found in any of our refereed publications. We will follow this with a description of the techniques that were developed to remove the adsorbed material from the P α MS shells. A key consideration in the development of the techniques used was the necessity of not simultaneously degrading the greatly improved sphericity the PAA provides.

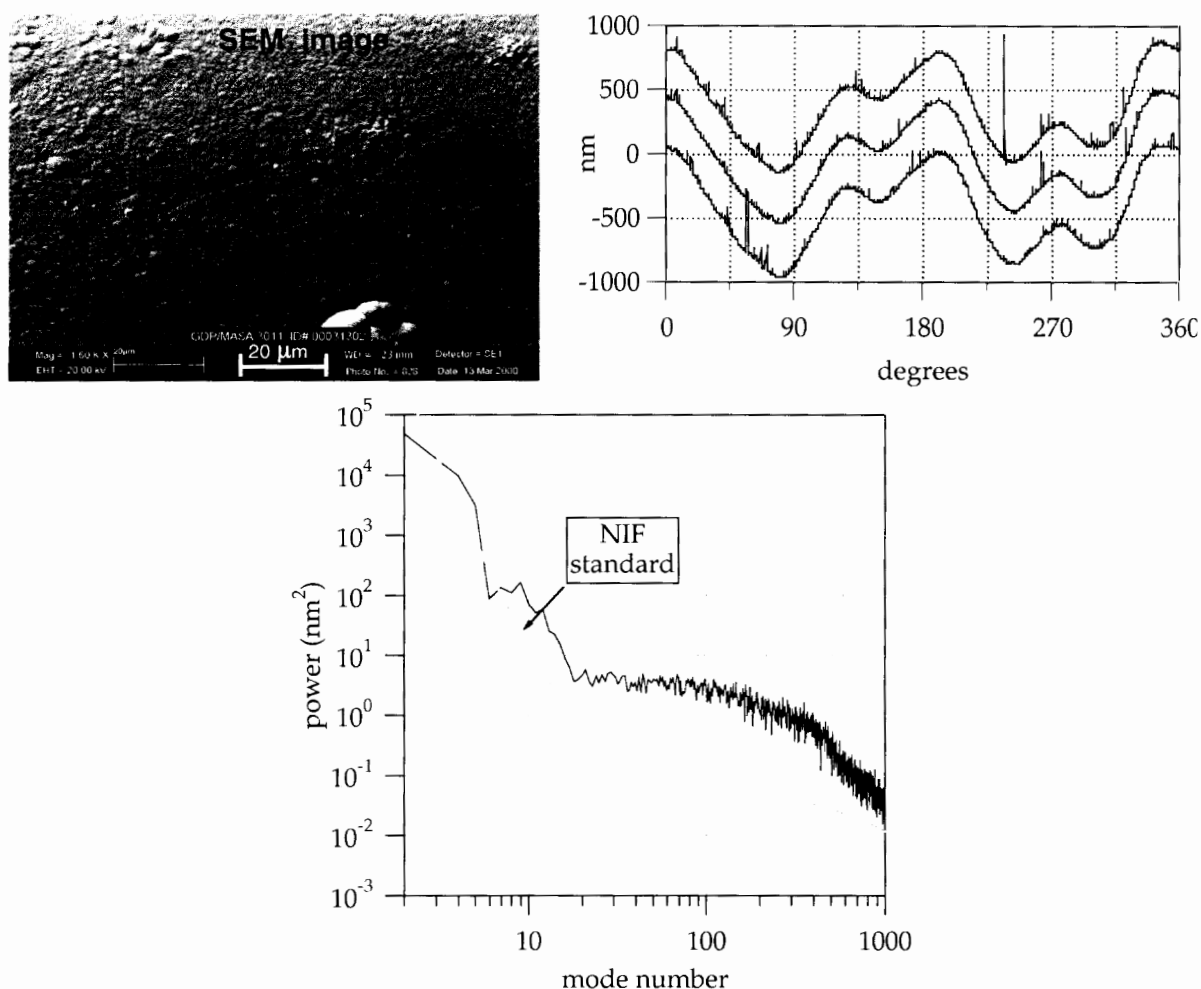


Figure 2. At the top left is shown a SEM image of a 55 μm coating of GDP on top of a PAA prepared shell. At the right are representative equatorial traces that show numerous “spikes” due to dome formation. At the bottom is the shell power spectrum which shows significantly enhanced power at the mid to high modes.

II. MATERIALS

A. Purification.

a) Fluorobenzene was freshly distilled at 85 C.

b) 50-100 g of 400,000 molecular weight P α MS is dissolved in one liter of toluene in a two liter flask. The P α MS solution is washed with one liter of water by stirring with a magnetic stirrer overnight, and then after phase separation the water is removed by suction via a cannula. This washing process is repeated until the toluene solution is clear and not hazy. This clear P α MS solution is filtered using 0.8 μm pore size PTFE filter, and then the P α MS is reprecipitated in ethanol. The reprecipitated P α MS is rinsed three times with ethanol. The P α MS is then dried in a vacuum oven at 40-50 C and then stored under vacuum below -20 °C. The water washing is done to remove any trace of lithium hydroxide originating in the synthesis of the P α MS from BuLi.

The presence of this lithium hydroxide causes vacuoles to form in the shell wall. The storage at -20 °C under vacuum is done to prevent degradation, since there is some evidence that 6-12 month old P α MS powder is more prone to forming vacuoles, even if the lithium has been removed.

B. Solutions.

a) 18 g P α MS is dissolved in 82 g distilled fluorobenzene to make an 18 wt% solution, which is then pressure filtered using 0.45 μ m pore size PTFE filter. This P α MS solution must be stored in a refrigerator until used within a week. We have some evidence that this solution even if stored in a refrigerator for 1-3 months is more prone to making vacuoles. Fresh solution makes shells with very few vacuoles.

b) 2 g 1,000,000 molecular weight PAA is dissolved in four liters of deionized water using a propeller stirrer for one week at room temperature to make a 0.05 wt% solution. The PAA solution is twice pressure filtered using an 8 and then 3 μ m pore size polycarbonate filter. The PAA solution viscosity is measured to be 12.8 to 13.3 cP at room temperature.

c) 120 g PVA is dissolved in four liters of deionized water using a magnetic stirrer for 3 hours at 90 C to make a 3 wt% solution. The PVA solution is vacuum filtered using a 0.2 μ m pore size PTFE filter.

III. BASIC PROCESS

A. Microencapsulation

The droplet generator is shown in Figure 3.

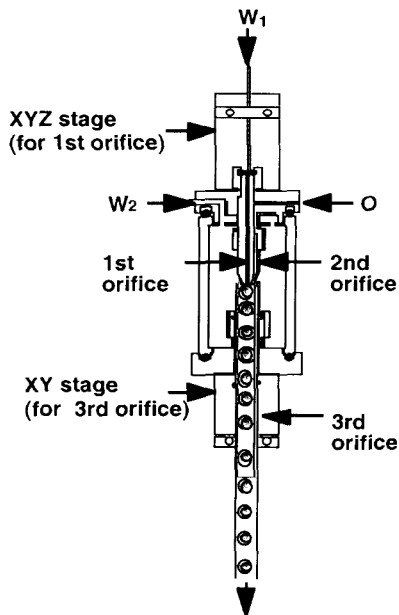


Figure 3. Droplet generator.

The generator dimensions are as follows:

First orifice: Tip of stainless steel tube OD 0.5 mm, ID 0.3 mm

Inlet of stainless steel tube OD 3.2 mm, ID 2.8 mm

Second orifice: Tip of shaped glass needle ID 0.7 to 1 mm

Base of glass tube OD 6 mm, ID 4 mm held by Teflon swagelock

Third orifice: Straight glass collection tube OD 6 mm, ID 4 mm, connected by flexible tubing to bring shells to rotary flask.

Solvent delivery:

Inner Water Phase (W1)

Pump : Cole-Parmer Syringe pump (74900-00)

Syringe : 50 ml

Flow rate: 40 ml/h

Connection tube : Teflon 1/8 OD

Oil phase (O)

Pump : Cole-Parmer Syringe pump (74900-00)

Syringe : 50 ml

Flow rate: 8 - 10 ml/h

Connection tube : Teflon 1/8 OD

Outer Water Phase (W2)

Pump : Cole-Parmer Tube pump Model No 7553-70

Connection tube : Tygon,

Flow rate: 170 – 190 ml/min as measured by a flow meter calibrated to water. The actual flow rate is adjusted to control shell formation rate given the W1 and O flow rates.

Collection tube: FEP lined Tygon 1/4 ID

Shells formation rate: 150 –155/min

Rotary cylinder flask and stir speed

ID 100 mm, length 100 mm, 50 rpm

ID 125 mm, length 100 mm, 30 rpm

B. Curing Process

The detailed curing process is the critical new step in this process since it is coupled with removal of PAA debris from the outer shell surface, and we defer detailed discussion to Section IV.

C. Drying.

After curing, the shells are transferred to a one liter beaker. They are rinsed by decantation at least 10 times with deionized water. The thoroughly rinsed shells are then placed with 60 mL of water in a small glass bottle. 5 ml of isopropyl alcohol (IPA) is added to the wet shells and 60 ml water. After mixing, the bottle with shells is placed in an ultrasonic bath for 2-3 sec, and then allowed to sit overnight. This process is repeated daily to nucleate a small air bubble in the core water, at which time the shell will float. Typically a total of 30-40 ml IPA is added over 1-2 weeks until the good shells float to the surface and broken shells remain on the bottom. The good shells are then moved into a vacuum oven for 1-2 weeks at 30-35 C to remove all the core water.

IV. INVESTIGATION OF METHODS TO REMOVE PAA FROM THE SHELL SURFACE

A. Washing

Our first approach was to enhance the washing process of the fully cured shells. Typically the process involves several rinses with water. However we felt that we could take advantage of the carboxylic functionality of the PAA by washing with basic and acidic media. Such changes in pH should result in significant changes in the chain conformation of the polyelectrolyte, hopefully loosening it from the surface. Thus we subjected a set of shells to a wash cycle consisting of first pure water, followed by dilute NaOH, pure water, dilute HCl, and then finally pure water again. Shown in Figure 4 is a comparison of equatorial traces as well as AFM patch scans of a shell rinsed only with water with a shell subjected to the above wash sequence. Clearly there is some significant improvement, indicating some level of success. However attempts to improve the process by adding additional wash cycles did not lead to further improvement and thus we proceeded to explore the options below.

B. PVA/PAA combination process

We next turned to the use of PVA as an agent that might remove PAA or prevent it from depositing, since as described above we knew that PVA, even at much higher concentrations than those used for PAA, rinsed completely off leaving no deposits. Our first approach was to produce the W1/O compound droplet shell precursors using PVA in the W2 phase, and then replaced varying fractions of the PVA solution with PAA solution, as shown in Figure 5, before completing the cure using the rotary stir method⁸ at 25 °C. In this way we hoped to keep the oil surface covered with a PVA layer while the interfacial tension might be enhanced by the PAA. A number of PVA:PAA final concentration ratios were examined as shown in Table I.

The basic result as shown in Table I is that the OOR increased unacceptably. This is not surprising since if the PVA was in fact coating the oil phase surface one would expect the effect of the PAA in increasing the interfacial tension to be reduced. In Figure 6 are shown representative equatorial traces along with a power spectrum for a shell produced by this method. The decrease in the low mode symmetry is the major feature, but in addition there is still visible debris manifest in the form of small spikes on the equatorial traces.

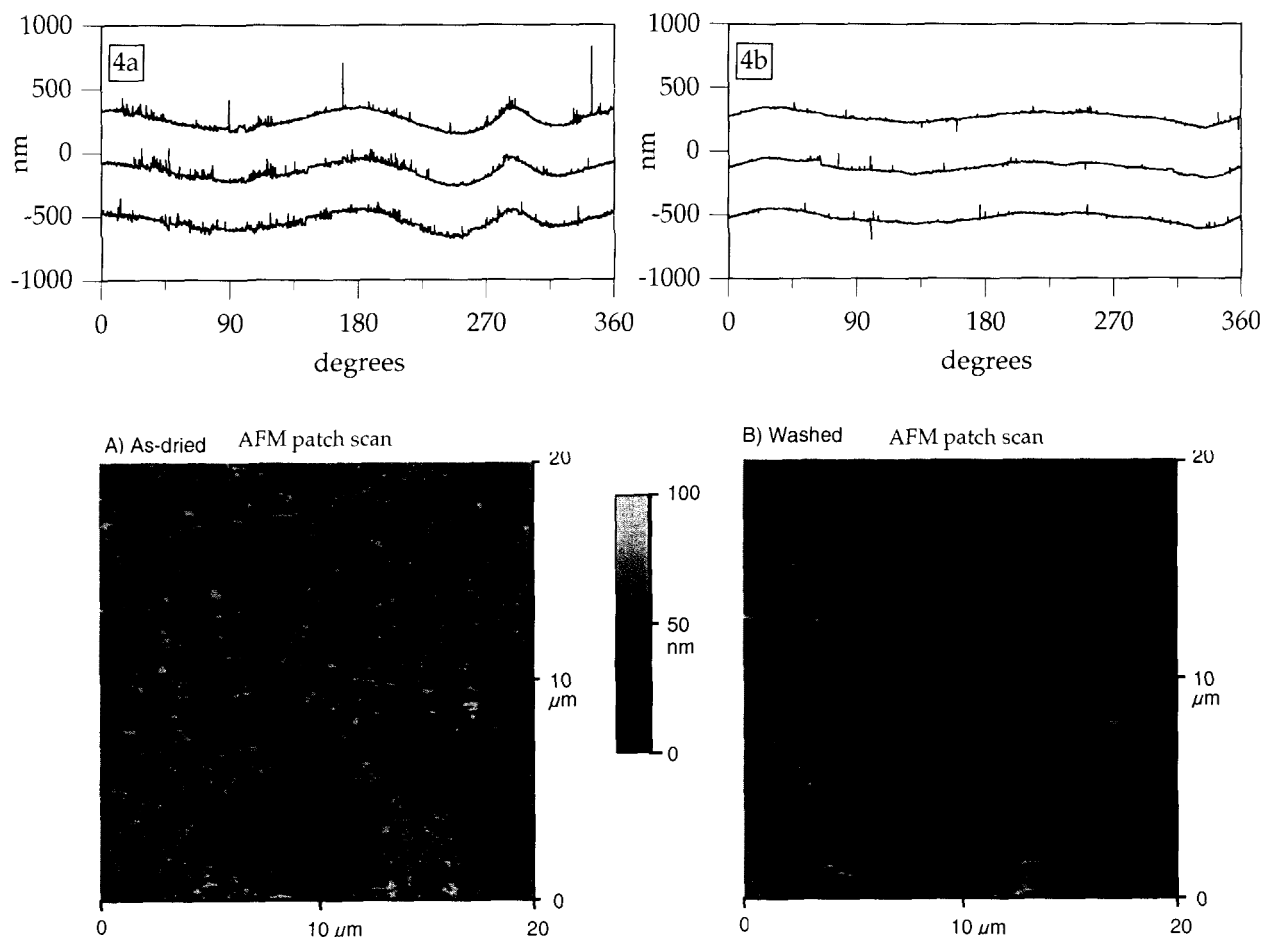


Figure 4. Shown are equatorial trace data and AFM patch scan pictures of an example shell rinsed only with water and one rinsed with the more aggressive base and acid treatment described in the text.

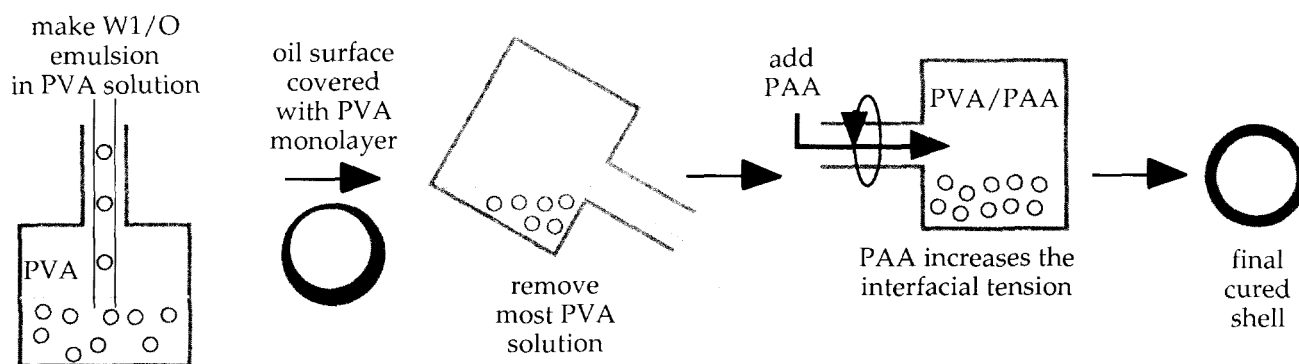


Figure 5. PVA/PAA combination process.

Table I. Conditions tested using the PVA/PAA combination process and the average OOR and NC.

Ratio PVA : PAA	trials	OOR μm	NC %
0.16% : 0.042%	2	3.9	1.8
0.25% : 0.038%	7	1.1	<1
0.33% : 0.033%	2	1.0	<1
0.50% : 0.025%	2	1.2	2.4

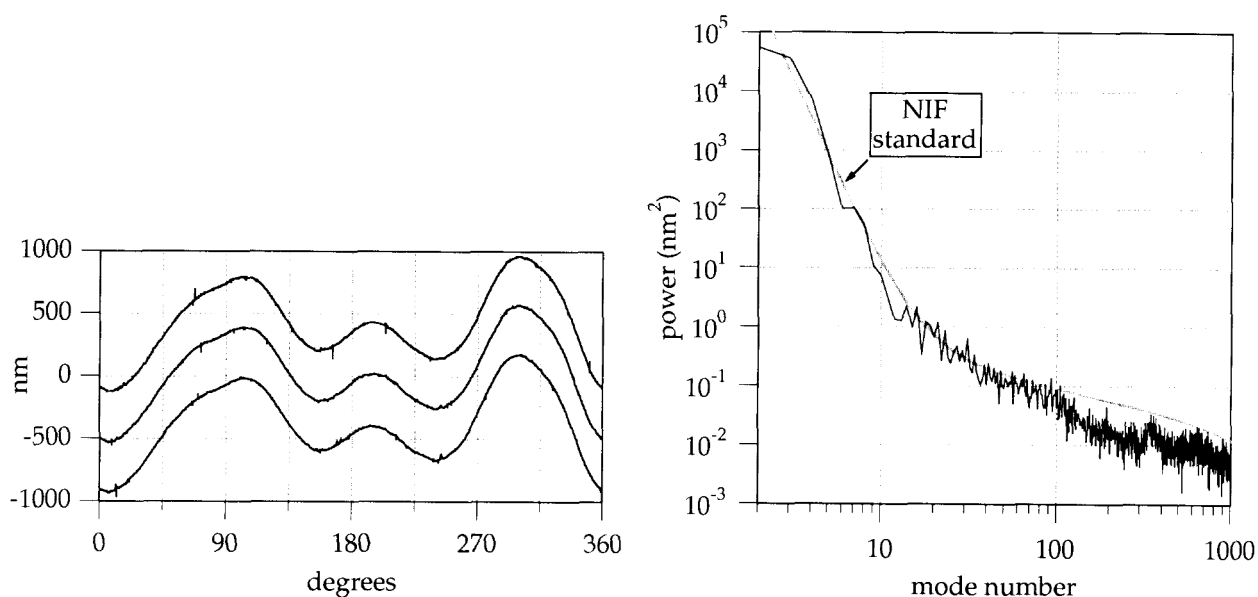


Figure 6. Representative traces and power spectrum from a shell prepared by the PVA/PAA combination method.

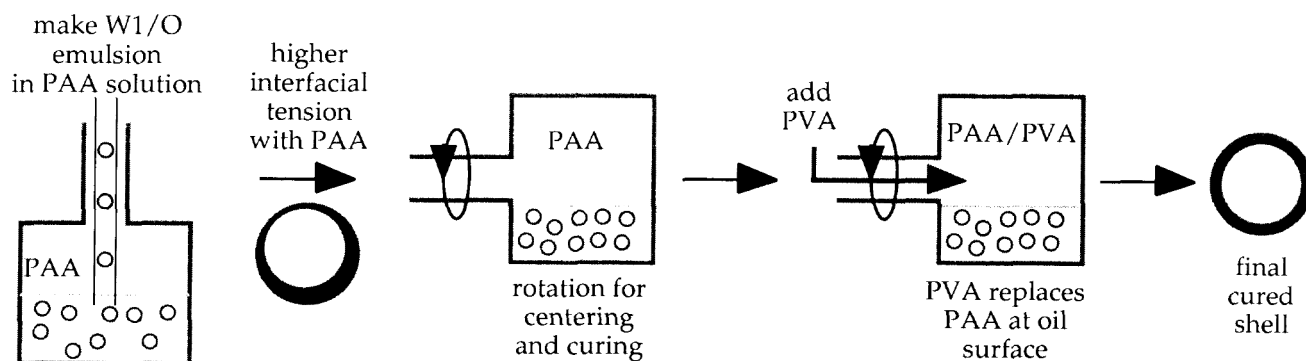


Figure 7. PAA/ PVA combination process.

C. PAA / PVA combination process

In this approach (see Figure 7) we attempted to set the shell sphericity with a PAA bath before adding PVA. Specifically W1/O compound droplets were prepared in a 0.05% PAA bath and were cured in this bath for a period of time to allow the viscosity of the oil phase to increase and set the low mode geometry of the shell,¹⁴ and then PVA was added to the bath in increments as shown in Table II. A detailed example of the process (6th line of Table II) is formation and partial curing in 240 ml PAA, addition of 10 ml 10% PVA after 23 h resulting in a net 0.4% PVA concentration in the bath, followed by addition of an additional 50 ml of 10% PVA after the 42 h resulting in a 2 wt% PVA concentration in the bath.

We found that the shell OOR was sensitive to the time of the first addition, short times resulting in greater OOR's as expected. In general, however, the approach was very effective in both maintaining shell sphericity and improving the surface finish of the shells. Representative equatorial traces and a power spectrum for the example condition detailed above are shown in Figure 8. There was some difficulty with reproducibility, in part because the cure time for each batch depends to some extent on the number of shells produced.

Table II. Conditions tested using the PAA/PVA combination process. All NC were less than 1%.

Time(h) of PVA addition and resultant wt% PVA						trial	OOR μm
1 st	PVA%	2 nd	PVA%	3 rd	PVA%		
4	0.3	24	0.7	48	1.3	2	2.3
6	0.3	24	0.7	48	1.3	2	1.0
7	0.3	24	0.7	48	1.3	2	1.0
26-28	0.3	45-47	1.0	53	2.0	4	1.1
10-14	0.3	22-26	2.0	-	-	6	0.9
22-25	0.3	42-48	2.0	-	-	12	0.8
29-31	0.5	45-48	0.9	-	-	6	1.1
41-43	0.3	65-67	2.0	-	-	4	0.7
17-19	2.0	-	-	-	-	4	0.6
22	2.0	-	-	-	-	2	1.0
22-33	2.0	54	3.0*	-	-	2	0.9

* all PAA removed prior to addition of 3% PVA

Table III. Conditions tested using the PVA exchange process and the resultant average OOR and NC.

Cure times			OOR μm	NC %
PAA(h)	PVA(h)	trial		
25-27	51	4	0.7	<1
28-30	48	8	0.6	<1

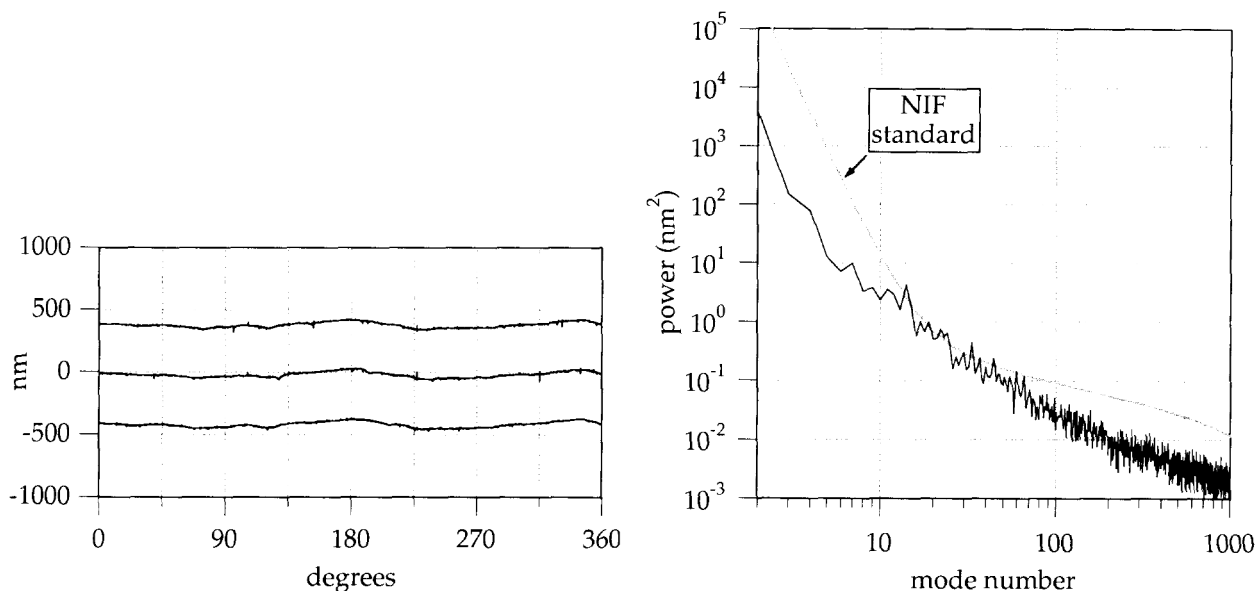


Figure 8. Representative traces and power spectrum from a shell prepared by the PAA/PVA combination method.

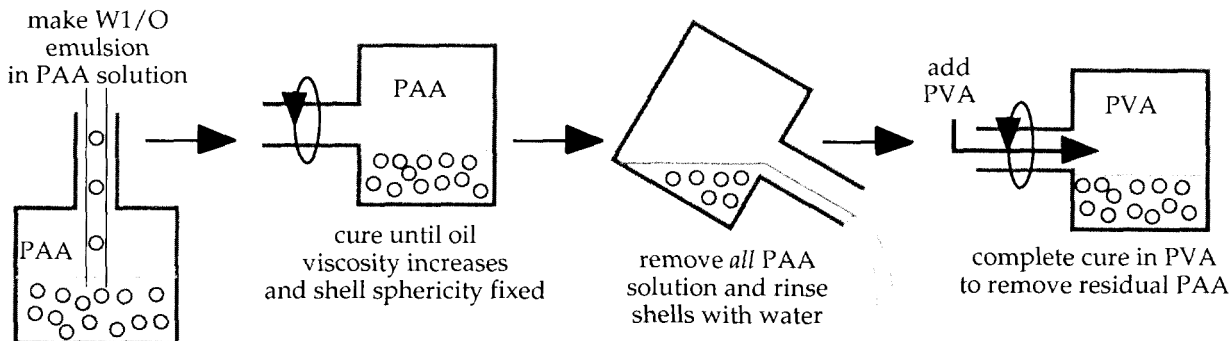


Figure 9. PVA exchange process

D. PVA exchange method

Noting our success in adding PVA to the PAA bath to displace residue from the surfaces and our success in preserving the basic shell symmetry by waiting until the oil phase viscosity had increased sufficiently, our next approach was to replace all of the PAA with high concentration PVA after an initial curing period as shown in Figure 9. Thus for example (1st line in Table III) the compound droplets are cured for 27 h in 0.05 wt% PAA and then the PAA is decanted off, the shells rinsed gently with water, and then 3 wt% PVA is added as the bath fluid and the curing continued in the rotary bath for an additional 2 days.

Representative traces and the power spectrum for a typical shell prepared by this method are displayed in Figure 10. The resulting shells are both spherical and reasonably free of surface debris. As a confirmatory test we show in Figure 11 a surface patch SEM image (compare with Figure 2) along with representative equatorial traces and the power spectrum of a typical PVA exchange process shell that has been overcoated with 14 μm of GDP and then pyrolyzed to produce a GDP shell.

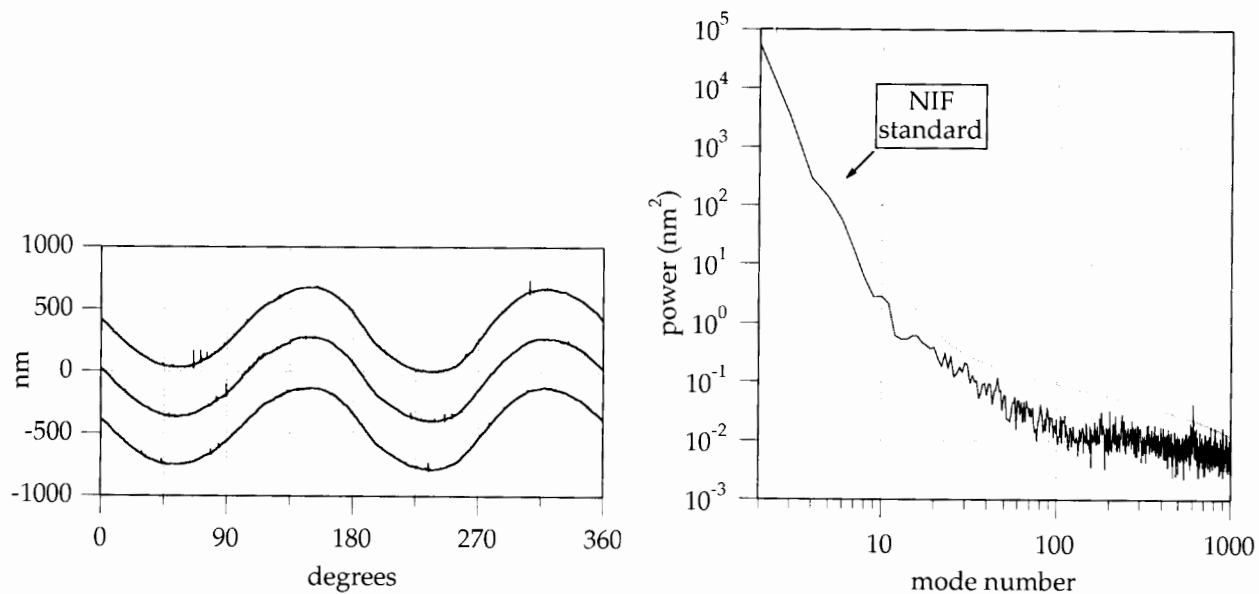


Figure 10. Representative traces and a power spectrum from a shell prepared by the PVA exchange method.

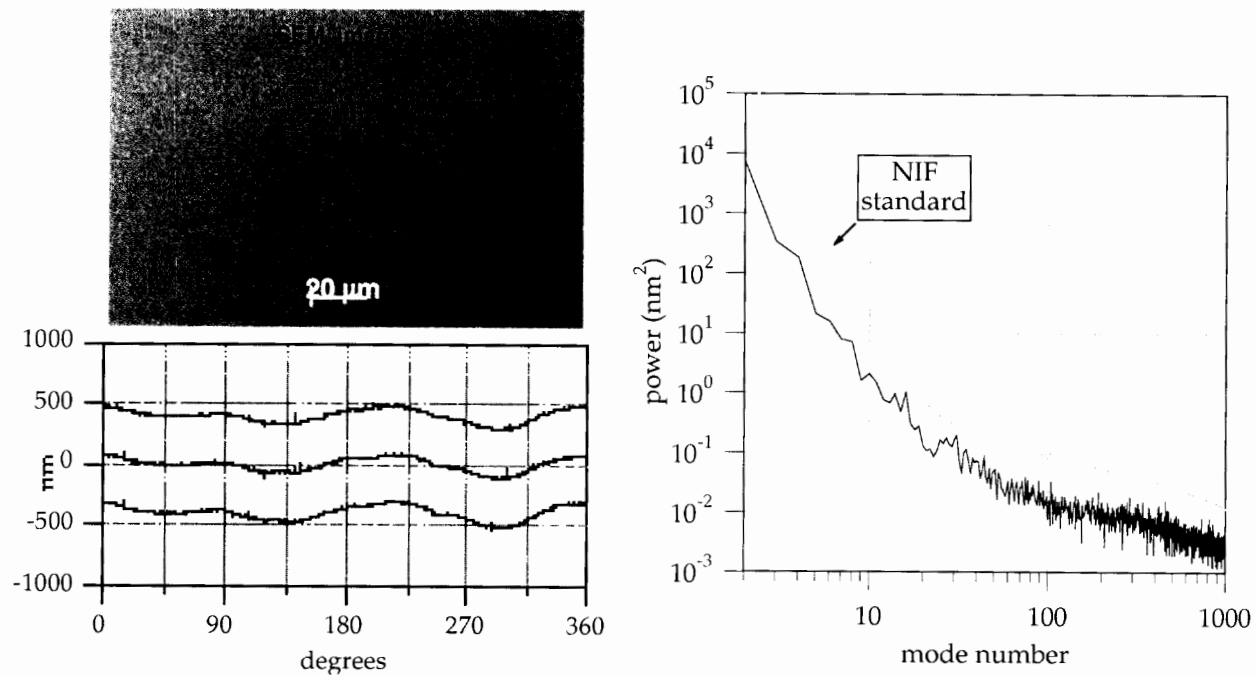


Figure 11. At the top left is shown a SEM image of a GDP shell prepared from a PVA exchange method PαMS mandrel. Below it are representative equatorial traces and to the right the power spectrum.

V. DISCUSSION AND SUMMARY

We have shown that PVA is effective at removing adsorbed PAA from the surfaces of P α MS shells. Further we have demonstrated that the fundamental shell symmetry, primarily the mode 2 OOR and NC, can be fixed by an initial formation and cure in PAA until the oil phase is viscous enough to resist distortion. What is not entirely clear is why PVA is effective. Let us present several possibilities. There are several interactions to consider. First there are the relative strengths of the interactions of PVA and PAA with the oil phase and relatively nonpolar (compared with water) curing shell surface. Second there are the interactions of the polymers with the aqueous media, and third there are the possible interactions of the polymers with each other. Perhaps the most logical explanation is that the interactions of PVA with the shell surface are in net more favorable than those of PAA, and thus the PAA is displaced. The difficulty with this line of reasoning is that the PVA appears to be relatively easily washed off the fully cured shells with water while the PAA is not. If the pure interaction strength with the surface is not the primary issue, then another view is that the driving force is basically a mass action argument. It must be remembered that the PVA concentration is up to 3 wt% while the PAA concentration is only 0.05 wt% initially, much less in the PVA exchange method described above. Thus even if the PAA/oil phase interaction is stronger, the large excess of PVA predominates. An additional consideration that might help explain the action of PVA is as follows. Though reasonably soluble in water, PVA nevertheless has some non-polar character. PAA is certainly more polar in nature than PVA, but still less than water. It is possible that especially at high PVA concentrations it is favorable for the high molecular weight PAA to effectively complex in solution through a combination of hydrogen bonding and nonpolar interactions the much lower molecular weight PVA, the net effect being to draw PAA off the surface. Such complex formation may increase the entropy of both species relative to their isolated state in water, and likewise one would expect that the desorbed PAA molecule with its huge molecular weight would be entropically more happy and that this might help pay for an enthalpic desorption penalty. These speculations are not easily testable but rather are meant to provide food for thought as we continue to refine the process of producing high symmetry P α MS mandrels.

In summary we have improved the production process for P α MS mandrels by utilizing a PAA/PVA combination process. Our best and most reproducible results come when we allow the initial compound droplets to cure and stiffen in a 0.05 wt% PAA rotary bath for about 24 h to set the overall sphericity, and then replace the PAA with 3 wt% PVA for an additional 2 days of treatment in the rotary bath. The advantages of PAA for low mode sphericity are maintained, and the resulting P α MS shells and GDP shells made from them meet or exceed the target surface design requirements at all modes.

ACKNOWLEDGEMENT

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10. Out-of-round is defined as the difference between the maximum and minimum radius.
11. Non-concentricity is the offset of the center of the outside surface from the inside surface, normalized to the wall thickness; it must be less than 5% in the mandrel to achieve uniform walls in the shell formed on it.

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